

OCCURRENCE OF HERBICIDE DEGRADATION COMPOUNDS IN STREAMS AND GROUND WATER IN AGRICULTURAL AREAS OF SOUTHERN GEORGIA, 2002

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Abstract. Water samples were collected during 2002 from 2 streams and 28 wells located in agricultural areas in southern Georgia and analyzed for more than 180 pesticides (including herbicides, insecticides, and their degradation compounds). The most frequently detected pesticides in stream samples were the herbicide degradation compounds metolachlor ethane sulfonic acid (ESA) (74 percent of samples), metolachlor oxanilic acid (OA) (61 percent), and alachlor ESA (61 percent). In contrast, the parent compounds, metolachlor and alachlor, were not detected in stream samples (at a reporting level of 0.05 micrograms per liter [$\mu\text{g/L}$]). Atrazine was detected in 45 percent of stream samples; and the atrazine degradation compound, deethyldeisopropylatrazine, was detected in 13 percent of stream samples. In ground water, metolachlor ESA (67 percent of samples), alachlor ESA (48 percent), and metolachlor OA (33 percent) were the most frequently detected pesticides. In contrast, metolachlor was detected in only 7 percent of ground-water samples and alachlor was not detected in any ground-water samples. Concentrations of metolachlor did not exceed 0.13 $\mu\text{g/L}$ in ground water; however, metolachlor ESA concentrations were as high as 19 $\mu\text{g/L}$ and metolachlor OA concentrations were as high as 4.42 $\mu\text{g/L}$ in ground water. The higher detection rates and higher concentrations of the metolachlor and alachlor degradation compounds relative to their parent compounds, highlight the importance of including herbicide degradation compounds in water-quality assessments to more fully evaluate the environmental fate of herbicides in hydrologic systems.

INTRODUCTION

Ground-water and stream samples were collected during 2002 to characterize water quality in agricultural areas in southern Georgia as part of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) program. The primary objectives of the

NAWQA program are to: (1) describe the condition of the Nation's stream and ground-water resources, (2) examine long-term trends in water-quality conditions, and (3) evaluate the human and natural processes that control water quality (Gilliom and others, 1995). Twenty-eight wells were installed in the surficial aquifer adjacent to agricultural fields in southern Georgia (Fig. 1), and ground-water samples were collected from January through May 2002. Twelve stream samples were collected from the Little River from February through May 2002 (flow ceased in the Little River in May), and 29 samples were collected from the Withlacoochee River from February through September 2002 (Fig. 1). The Little River is an intermittent stream that drains a small agricultural basin (129 square miles [mi^2]) and is a tributary to the Withlacoochee River. The Withlacoochee River basin covers an area of 2,400 mi^2 of mixed land use.

The herbicide degradation compounds of metolachlor, alachlor, and atrazine have been detected more frequently and at higher concentrations than their parent compounds in streams and ground water in Iowa (Kalkhoff and others, 1998; Kolpin and others, 1997) and New York (Eckhardt and others, 2001; Phillips and others, 2000). These findings highlight the importance of analyzing degradation compounds of herbicides to assess the occurrence and environmental fate of herbicides in hydrologic systems. As a result, degradation compounds of selected herbicides were analyzed in ground water and streams in selected agricultural areas across the Nation for the NAWQA program during 2002, including southern Georgia.

Methods

Water samples were collected and processed according to USGS methods (Wilde and others, 1998; 1999). Samples were analyzed at the USGS National Water Quality Laboratory in Denver, Colorado, for more than 180 pesticides and degradation compounds, including alachlor, metolachlor, atrazine, deethylatrazine

(DEA), deethyldeisopropylatrazine, deisopropylatrazine (DIA), and simazine (Furlong and others, 2001; Sandstrom and others, 2001; Zaugg and others, 1995). Samples also were analyzed for 10 chloroacetanilide herbicide degradation compounds—acetochlor ethane sulfonic acid (ESA), acetochlor oxanilic acid (OA), alachlor ESA, alachlor OA, dimethenamid ESA, dimethenamid OA, flufenacet ESA, flufenacet OA, metolachlor ESA, and metolachlor OA—by the USGS Organic Geochemistry Research Group in Lawrence, Kansas (Lee and others, 2001).

Reporting levels for the various herbicides and herbicide degradation compounds focused on in this paper ranged from 0.006 to 0.05 micrograms per liter ($\mu\text{g/L}$). Because differences in reporting levels influence the interpretation of detection frequencies, a common detection threshold of 0.05 $\mu\text{g/L}$ is used for the frequency of detection for all herbicides and herbicide degradation compounds discussed in this paper.

RESULTS AND DISCUSSION

Streams

The degradation compounds of metolachlor and alachlor were detected frequently in stream samples, although neither metolachlor nor alachlor were detected in stream samples at concentrations above the 0.05- $\mu\text{g/L}$ reporting level. The most frequently detected pesticides in stream samples were the herbicide degradation compounds metolachlor ESA (74 percent of samples), metolachlor OA (61 percent), and alachlor ESA (61 percent) (Table 1). Metolachlor ESA and metolachlor OA were each detected in 100 percent of the samples collected from the Little River during February through May 2002—both degradation compounds were detected only in the Withlacoochee River from February through mid-May 2002 (Little River ceased to flow in May). Concentrations of metolachlor ESA and metolachlor OA were greater in samples from the small agricultural Little River basin than in samples from the larger mixed land-use Withlacoochee River basin—metolachlor ESA concentrations ranged from 0.83 to 1.47 $\mu\text{g/L}$ in Little River samples and from 0.22 to 0.58 $\mu\text{g/L}$ in Withlacoochee River samples. Metolachlor OA ranged from 0.13 to 0.28 $\mu\text{g/L}$ in the Little River and from 0.05 to 0.13 $\mu\text{g/L}$ in the Withlacoochee River. Concentrations are probably higher in the Little River because of the higher proportion of agricultural land use in its basin relative to the Withlacoochee River basin. The higher concentrations of metolachlor ESA relative to metolachlor OA and the parent compound, metolachlor, that were observed in this study also have been documented in previous investigations, and is related to the greater persistence of metolachlor ESA in the environment relative to the other compounds (Kalkhoff and others, 1998).

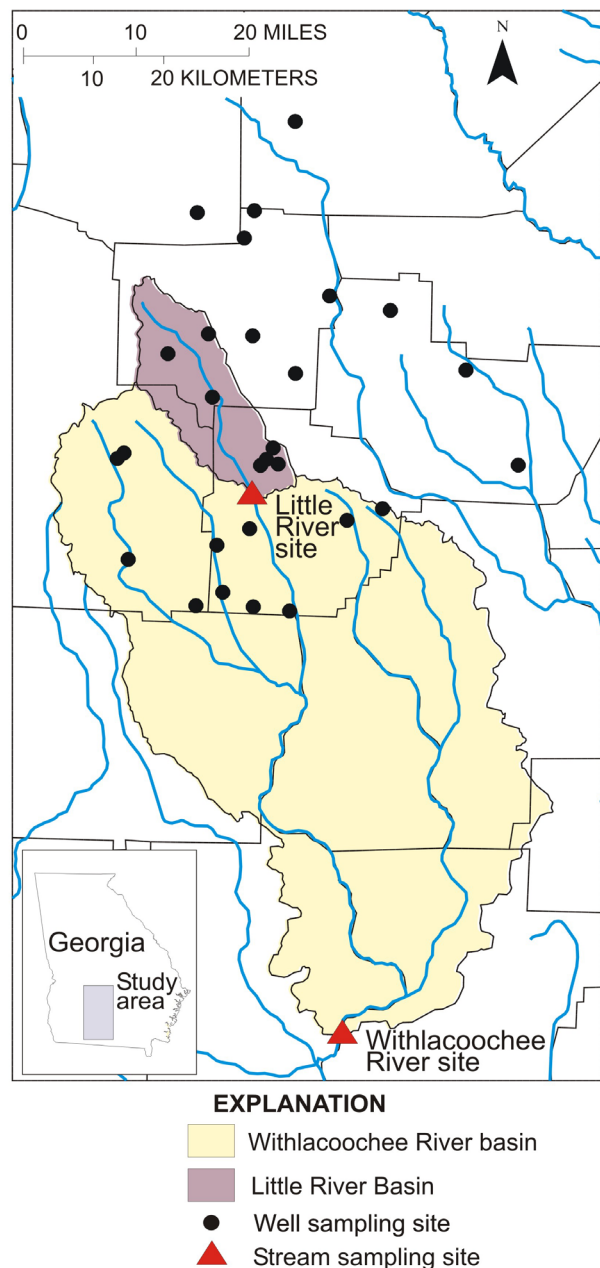


Figure 1. Location of sampling sites in southern Georgia.

Table 1. Detection frequencies and maximum concentrations for atrazine, metolachlor, alachlor, and simazine and their degradation compounds in ground water and stream water

[Based on common detection level of 0.05 micrograms per liter; GW, ground water; SW, stream water; n, number of samples; concentrations in micrograms per liter; ND, not detected]

Herbicide or degradation compound	GW percent detections n=28	GW maximum concentration	SW percent detections n=31	SW maximum concentration
Atrazine	0	0.022	45	0.90
Deethylatrazine (DEA)	0	ND	0	ND
Deethyldeisopropylatrazine	0	ND	13	0.24
Deisopropylatrazine (DIA)	0	ND	0	ND
Metolachlor	7	0.13	0	ND
Metolachlor ESA	67	19	74	1.47
Metolachlor OA	33	4.42	61	0.28
Alachlor	0	ND	0	ND
Alachlor ESA	48	5.86	61	0.21
Alachlor OA	18	1.16	0	ND
Simazine	0	ND	10	0.25

Alachlor was not detected in any of the stream samples collected; however, alachlor ESA was detected in 61 percent of stream samples. Similar to the metolachlor degradation compounds, alachlor ESA was detected in 100 percent of the Little River samples, but was detected only in the Withlacoochee River samples during the period when the Little River was flowing. Concentrations of alachlor ESA were slightly higher in the Little River compared to the Withlacoochee River—concentrations ranged from 0.11 to 0.21 µg/L in the Little River compared to 0.05 to 0.11 µg/L in the Withlacoochee River.

The most frequently detected parent compounds in the stream samples were atrazine (45 percent of samples) and simazine (10 percent) (Table 1). The maximum atrazine concentration in stream samples was 0.90 µg/L, and the maximum simazine concentration was 0.25 µg/L (Table 1). Deethyldeisopropylatrazine, the only atrazine degradation compound detected in the stream samples, was detected less frequently (13 percent) than its parent compound and at lower concentrations (maximum concentration 0.24 µg/L; Table 1).

Ground Water

Frequently detected pesticides in ground water were metolachlor ESA (detected in 67 percent of samples), alachlor ESA (48 percent), metolachlor OA (33 percent), and alachlor OA (18 percent) (Table 1). Although the detection frequencies of these compounds in ground water are slightly lower than the detection frequencies in stream samples, the maximum concentrations are much higher in ground water compared to stream water. For example, the maximum concentration of metolachlor ESA in ground water was 19 µg/L compared to a maximum of 1.47 µg/L in stream water, and the maximum concentration of metolachlor OA was 4.42 µg/L in ground water compared to 0.28 µg/L in streams (Table 1). Metolachlor was detected in 7 percent of the ground-water samples but was not detected in any of the stream samples. The maximum concentration of metolachlor in ground water was 0.13 µg/L—an order of magnitude lower than the maximum concentration of its degradation compound, metolachlor ESA (19 µg/L) (Table 1). Similar to the results for stream samples, metolachlor ESA concentrations in ground-water samples were higher than metolachlor OA or the parent compound, metolachlor.

These results are similar to those found in Iowa (Kalkhoff and others, 1998), but differ in that the maximum concentrations of metolachlor ESA in ground-water samples are an order of magnitude higher than concentrations in stream samples. Differences between these study results and the results from the Iowa study could be related to differences in the types of wells sampled (low-capacity monitoring wells were sampled in this study compared to a combination of monitoring wells and municipal supply wells sampled in Iowa (Stephen J. Kalkhoff, U.S. Geological Survey, oral commun., 2003), and to the lower percentage of stream basin areas in agricultural land use. In this study, the Little River Basin and the Withlacoochee River basin are approximately 67 and 56 percent agricultural land use, respectively (Hatzell, 1996), whereas agricultural land use in the Iowa basins ranged from 87 to 96 percent (Becher and others, 2001).

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